

REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-00-

8

Public reporting burden for this collection of information is estimated to average 1 hour per response, including gathering and maintaining the data needed, and completing and reviewing the collection of information, including suggestions for reducing this burden, to Washington Headquarters, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Project, Washington, DC 20503.

data sources,
aspect of this
215 Jefferson
0503.

8461

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED Final - 1 April 1999 to 30 November 1999
4. TITLE AND SUBTITLE Molecular Nonlinear Optical Susceptibilities in Condensed Phases		5. FUNDING NUMBERS F49620-99-1-0226
6. AUTHOR(S) Dr. Shaul Makumel Department of Chemistry		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Rochester Rochester, NY 14627-0216		8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NL 801 North Randolph Street, Rm 732 Arlington, VA 22203-1977		10. SPONSORING/MONITORING AGENCY REPORT NUMBER
11. SUPPLEMENTARY NOTES		
12a. DISTRIBUTION AVAILABILITY STATEMENT APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED		12b. DISTRIBUTION CODE
13. ABSTRACT (Maximum 200 words) A unified microscopic theoretical framework for the calculation of optical excitations in molecular and semiconductor materials was developed. The hierarchy of many-body density matrices for a pair-conserving many-electron model and the Frenkel exciton model was rigorously truncated to a given order in the radiation field. Closed equations of motion were derived for five generating functions representing the dynamics up to third order in the laser field including phonon degrees of freedom as well as all direct and exchange-type contributions to the Coulomb interaction. By eliminating the phonons perturbatively, we obtained equations that, in the case of the many-electron system, generalize the semiconductor Bloch equations, are particularly suited for the analysis of the interplay between coherent and incoherent dynamics including many-body correlations, and lead to thermalized exciton (rather than single-particle) distributions at long times. A complete structural equivalence with the Frenkel exciton model of molecular materials was established.		
14. SUBJECT TERMS Molecular, Optical		15. NUMBER OF PAGES 15
		16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT Unclass	18. SECURITY CLASSIFICATION OF THIS PAGE Unclass	19. SECURITY CLASSIFICATION OF ABSTRACT Unclass
20. LIMITATION OF ABSTRACT		

20000929 053

DQC QUALITY INSPECTED 4

FINAL TECHNICAL REPORT

Molecular Nonlinear Optical Susceptibilities in Condensed Phases
(F49620-99-1-0226)

for the Period

December 1, 1995 - March 31, 1999
Extension period April 1, 1999 - November 30, 1999

Submitted to the Air Force Office of Scientific Research

by

Shaul Mukamel
University of Rochester
Department of Chemistry
Rochester, NY 14627-0216

STATUS OF EFFORT

Optical spectroscopy of conjugated molecules was described by using collective electronic coordinates, which represent the joint dynamics of electron-hole pairs. The approach relates the optical signals directly to the dynamics of charges and bond orders (electronic coherences) induced by the radiation field and uses only ground-state information, thus avoiding the explicit calculation of excited molecular states. The resulting real-space picture is reminiscent of the normal-mode analysis of molecular vibrations and offers a unified framework for the treatment of other types of systems including semiconductor nanostructures and biological complexes.

Collective-oscillator representation of electronic excitations in large molecules was developed. Direct calculation of dominant oscillators was carried out using the DSMA (Density Matrix Spectral Moment Algorithm). Using this approach real-space analysis of electronic coherence sizes underlying the optical response was performed.

Applications were made to collective optical excitations of poly(p-phenylenevinylene) (PPV) oligomers, stilbenoid aggregates, and acceptor-substituted carotenoids. Origin, scaling, and saturation of second order polarizabilities in donor/acceptor polyenes was studied. Vibrational and solvent effects in resonant and off-resonant optical spectroscopy were investigated. Electronically resonant and off-resonant polarizabilities were calculated. Optical response femtosecond spectroscopies and localized electronic excitations in phenylacetylene dendimers were studied.

ACCOMPLISHMENTS/NEW FINDINGS

The grant resulted in 83 publications which are listed below.

Nonlinear Optics of Molecular and Semiconductor Nanostructures: A Common Perspective

A unified microscopic theoretical framework for the calculation of optical excitations in molecular and semiconductor materials was developed. The hierarchy of many-body density matrices for a pair-conserving many-electron model and the Frenkel exciton model was rigorously truncated to a given order in the radiation field. Closed equations of motion were derived for five generating functions representing the dynamics up to third order in the laser field including phonon degrees of freedom as well as all direct and exchange-type contributions to the Coulomb interaction. By eliminating the phonons perturbatively we obtained equations that, in the case of the many-electron system, generalize the semiconductor Bloch equations, are particularly suited for the analysis of the interplay between coherent and incoherent dynamics including many-body correlations, and lead to thermalized exciton (rather than single-particle) distributions at long times. A complete structural equivalence with the Frenkel exciton model of molecular materials was established.

Multiple Exciton Coherence Sizes in Biological Antenna Complexes

The pump-probe signal from the light-harvesting antenna LH2 of purple bacteria was analyzed using a Green function expression derived by solving the nonlinear exciton-oscillator equations of motion (NEE). A microscopic definition of the exciton mean free path (L_f) and localization size (L_p) was given in terms of the off-diagonal elements of the exciton Green function and density matrix, respectively. Using phonon-induced (homogeneous) and disorder-induced (inhomogeneous) line widths compatible with superradiance measurements, we find that at 4.2 K the localization size is L_p and that the shift • • between the positive and negative peaks in the differential absorption is determined by a different effective size $L_f/2 = 5.6$ associated with the exciton mean free path. Our model further predicts the recently observed superradiance coherence size determined by L_p . A real-space formulation of time-resolved fluorescence of molecular aggregates was developed using the one-exciton density matrix $\rho(t)$ of the optically-driven system. A direct relationship was established between the superradiance enhancement factor L_s , and the exciton coherence size L_p associated with the off-diagonal density matrix elements in the molecular representation. Various factors which affect the latter, including finite temperature, energetic disorder, coupling with phonons, and polaron formation were explored. The theory was applied for the interpretation of recent measurements in the B850 systems of the LH2 photosynthetic complexes. Femtosecond spectroscopies of chlorophyll dimers and the LH2 antenna complex were calculated using a theory that incorporates the effect of two-exciton states, static disorder and coupling of excitons to phonons with an arbitrary spectral density. Applications were made to pump-probe and echo peak-shift measurements in the B820 dimers, and to fluorescence depolarization in the B850 system of the LH2 antenna of purple bacteria.

Two-pulse four-wave-mixing signals from molecular aggregates, including effects of two-exciton states, static disorder, and exciton-phonon interaction represented by arbitrary spectral densities were calculated. Three types of contributions to the signal were identified. The first, reflecting exciton self-correlation, is similar to the photon echo from disordered two-level systems and dominates the signal for long time-delays. The second is related to correlations of one-exciton states, whereas the third reflects correlations between one- and two-exciton states. The information gained by completely resolving the signal field (both amplitude and phase) was analyzed using Wigner spectrograms.

Two-Dimensional Real-Space Analysis of Optical Excitations in Acceptor-Substituted Carotenoids

Absorption spectra of substituted carotenoids with varying acceptor strength were analyzed using collective electronic normal modes obtained using the time-dependent Hartree—Fock (TDHF) technique combined with the INDO/S semiempirical Hamiltonian. Two-dimensional plots of the collective excitations in real-space show an *off-diagonal size* associated with relative motion of electron-hole pairs created upon optical excitation and a *diagonal size* representing the pair's center of mass motion. By

varying the polyene chain length we show that the response of symmetric molecules is controlled by “bulk delocalized excitations with coherence size ~ 12 double bonds, whereas the response of short polar molecules is dominated by a localized “charge-transfer” excitation created at the acceptor end with coherence and diagonal lengths ~ 12 and ~ 17 double bonds, respectively.

Origin, Scaling, and Saturation of Second Order Polarizabilities in Donor/Acceptor Polyenes

Spatial coherence displayed in two-dimensional plots of the five electronic normal modes that dominate the optical response of poly (*p*-phenylene vinylene) oligomers with up to 50 repeat units (398 carbon atoms) in the 1.5- to 8-electronvolt frequency range suggests a saturation to bulk behavior at about five repeat units. Two-dimensional plots representing the changes in charge and bond-order distributions induced by the optical field were used to investigate the size-scaling of polarizabilities of donor/acceptor substituted elongated polyenes. The second order polarizability was shown to originate from localized regions at the donor/acceptor ends and therefore saturates to a constant value, independent on polyene size n , for large n . In contrast, the linear and cubic polarizabilities have coherence sizes that control the optical response and should be most valuable in the design of new optical materials.

Solvent Reorganization in Long-Range Electron Transfer: Density Matrix Approach

The dynamics of charge transfer from a photoexcited donor to an acceptor coupled through a bridge was investigated by using a correlation-function approach in Liouville space that takes into account solvent dynamics with an arbitrary distribution of time scales. The time- and frequency-resolved fluorescence spectrum from the acceptor was used to probe the scaling of the ET rate with bridge size. The crossover between the coherent tunneling (transfer) and the incoherent sequential (transport) regimes and its implications on the nature of ET process in DNA were discussed.

Multidimensional Femtosecond Spectroscopies of Vibrational Motions in Liquids: Semiclassical Expansion

Fifth and seventh order electronically off-resonant Raman spectroscopies in molecular liquids were investigated using a new semiclassical expansion of the optical response which applies for weak anharmonicities and low temperatures. The leading contribution can be calculated using classical equations of motion for nuclear wave packets, even when the system itself may be highly nonclassical. Two sources of nonlinearities which generate the

signal—the nonlinear dependence of the polarizability on nuclear coordinates and vibrational anharmonicities—are identified. Formal analogy between the present equations and the time-dependent Hartree-Fock equations used in electronic nonlinear spectroscopy suggest specific experimental signatures of the various nonlinearities.

Stilbenoid Dimers: Dissection of a Paracyclophane Chromophore

A series of paracyclophane derivatives that hold chromophores of varying conjugation lengths has been synthesized. These molecules mimic solid-state interactions in main-chain polychromophores and conjugated emissive polymers such as poly(*p*-phenylenevinylene) (PPV). Their optical properties give insight into the energetics of photoexcitations localized in a discrete chromophore relative to a state containing the through-space delocalized paracyclophane core. The observed trends in absorption, fluorescence and radiative lifetime of these compounds were reported and analyzed using collective electronic oscillators (CEO) representing the changes induced in the reduced single-electron density matrix upon optical excitation. Comparison of the CEO of the aggregates with the corresponding monomers using the two-dimensional plots provides an efficient method for tracing the origin of the various optical transition by identifying the underlying changes in the charge densities and bond orders. For some derivatives the emission is red-shifted from the “monomeric” compound and featureless, reminiscent of excimer qualities. The emissions of other molecules are similar to the “monomer” and display vibronic structure. Thus, for the smaller chromophores, emission occurs from a state containing the through-space delocalized paracyclophane core. In the situation where extended chromophores, with more stable excited states, are held together with the paracyclophane core, the photophysics of the individual chromophores dominates. The present analysis is relevant to the design and synthesis of organic molecules with desired optical properties.

Localized Electronic Excitations in Phenylacetylene Dendrimers

Electron-hole pairs created upon optical excitation of conjugated dendrimers (fractal antenna macromolecules) were shown to be localized within segments connected by benzene rings substituted at the meta-position. The absorption spectra of two families of dendrimers were analyzed using collective electronic normal modes representing the changes in charge and bond-order distributions induced by the optical field. The present approach may be used in the design of artificial light-harvesting antennae with controlled energy-funneling pathways.

Collective Coordinates for Semiclassical Femtosecond Dissipative Dynamics in Liouville Space

A semiclassical path-integral algorithm for propagating the reduced density matrix of a quantum-particle coupled to a harmonic bath with an arbitrary temperature and distribution in timescales was developed. Using a canonical transformation of the action in Liouville space, a unique prescription was provided for constructing collective bath

coordinates for a given nuclear spectral density. The number of relevant collective coordinates depends on the structure of the spectral density and increases at lower temperatures.

PUBLICATIONS

Published

1. "Photon Echoes in Impulsive Optical Spectroscopy of Phonons," J. A. Leegwater and S. Mukamel, *J. Chem. Phys.* **102**, 2365-2371 (1995).
2. "Real-Space Coupled-Oscillator Approach to the Radiative Decay of Conjugated Polymers," M. Hartmann, V. Chernyak and S. Mukamel, *Phys. Rev. B* **52**, 2528-2538 (1995).
3. "Level Correlations and Dephasing-Induced Resonances in Molecular Aggregates," V. Chernyak and S. Mukamel, *Physica Status Solidi*, **189**, 67-73 (1995).
4. "Nonlocal Electrodynamics of Arrays of Quantum Dots," L. Belleguie and S. Mukamel, *Phys. Rev. B* **52**, 1936-1947 (1995).
5. "Time-Dependent Density-matrix Functional in Liouville Space and the Optical Response of Many-electron Systems," V. Chernyak and S. Mukamel, *Phys. Rev. A* **52**, 3601-3621 (1995).
6. "Anharmonic Oscillator Representation of Nonlinear Optical Susceptibilities of a Charged Soliton, a Neutral Soliton and a Polaron in Conjugated Polymers," A. Takahashi and S. Mukamel, *J. Chem. Phys.* **103**, 7144-7155 (1995).
7. "Reduced Electronic Density Matrices, Effective Hamiltonians, and Nonlinear Susceptibilities of Conjugated Polyenes," G. Chen and S. Mukamel, *J. Chem. Phys.* **103**, 9355-9362 (1995).
8. "Generalized Sum Rules for Optical Nonlinearities of Many-Electron Systems," V. Chernyak and S. Mukamel, *J. Chem. Phys.* **103**, 7640-7644 (1995).
9. "Two-Exciton Collective Photon Echoes in Disordered Molecular Nanostructures," V. Chernyak and S. Mukamel, *Phys. Rev. Lett.* **74**, 4895-4898 (1995).
10. "Four-Wave Mixing and Luminescence of Confined Excitons in Molecular Aggregates and Nanostructures. Many-Body Green Function Approach," V. Chernyak, N. Wang, and S. Mukamel, *Physics Reports* **263**, 213-309 (1995).
11. "Size-Consistent Quasiparticle Representation of Nonlinear Optical Susceptibilities in Many-Electron Systems," V. Chernyak and S. Mukamel, *J. Chem. Phys.* **104**, 444-459 (1996).
12. "Nonlinear Polarizabilities of Donor-Acceptor Substituted Conjugated Polyenes," G. Chen and S. Mukamel, *J. Phys. Chem.* **100**, 11080-11085 (1996).
13. "Optical Stark Spectroscopy of Molecular Aggregates," S. Mukamel, P. Rott, and V. Chernyak, *J. Chem. Phys.* **104**, 5415-5423 (1996).

14. "Classical Chaos and Fluctuation-Dissipation Relations for Nonlinear Response," S. Mukamel, V. Khidekel, and V. Chernyak, *Phys. Rev. E* (Rapid Commun.) **53**, 1-4 (1996).
15. "Third-Order Optical Response of Intermediate Excitons with Fractional Nonlinear Statistics," V. Chernyak and S. Mukamel, *J. Opt. Soc. Am. B* **13**, 1302-1307 (1996).
16. "Intermolecular Electronic Coherences and Local Field Effects in Optical Spectra of PPV-Oligomer Dimers," T. Wagersreiter and S. Mukamel, *Chem. Phys.* **210**, 171-193 (1996).
17. "Semiclassical Path-Integral Approach to Nonlinear Spectroscopy," V. Khidekel, V. Chernyak, and S. Mukamel, *Femtoscience*, M. Chergui, Editor (World Scientific, Singapore) 507-514 (1996).
18. "The Coupled Electronic Oscillators Versus the Sum-Over-States Pictures for the Optical Response of Octatetraene," G. Chen, S. Mukamel, D. Beljonne and J. L. Bredas, *J. Chem. Phys.* **104**, 5406-5414 (1996).
19. "Wigner Spectrograms for Femtosecond Pulse-Shaped Heterodyne and Autocorrelation Measurements," S. Mukamel, C. Ciordas-Ciurdariu, and V. Khidekel, *IEEE J. of Quant Electr* **32**, 1278-1288 (1996).
20. "Linear and Nonlinear Optical Response of Dimethyl-Amino-Nitro-Stilbene (DANS): Coupled Oscillator Representation Versus Sum-Over-States Picture," D. Beljonne, J. L. Bredas, G. Chen, and S. Mukamel, *Chem. Phys.* **210**, 353-366 (1996).
21. "Effective Hamiltonian for Conjugated Polyenes Based on the Ground State Single-Electron Density Matrix," G. Chen and S. Mukamel, *Chem. Phys. Lett.* **258**, 589-594 (1996).
22. "Collective Coordinates for Nuclear Spectral Densities in Energy Transfer and Femtosecond Spectroscopy of Molecular Aggregates," V. Chernyak and S. Mukamel, *J. Chem. Phys.* **105**, 4565-4583 (1996).
23. "Collective Electronic Oscillators for Nonlinear Optical Response of Conjugated Molecules," S. Tretiak, V. Chernyak, and S. Mukamel, *Chem. Phys. Lett.* **259**, 55-61 (1996).
24. "Femtosecond Spectroscopic Signatures of Electronic Correlations in Conjugated Polyenes and Semiconductor Nanostructures," T. Meier and S. Mukamel, *Phys. Rev. Lett.* **77**, 3471-3474 (1996).
25. "Two-Exciton Spectroscopy of Photosynthetic Antenna Complexes: Collective Oscillator Analysis," O. Kuhn, V. Chernyak and S. Mukamel, *J. Chem. Phys.* **105**, 8586-8601 (1996).
26. Liquids," V. Khidekel, V. Chernyak, and S. Mukamel, *J. Chem. Phys.* **105**, 8543-8555 (1996).
27. "Optical Activity of Electronically Delocalized Molecular Aggregates: Nonlocal Response Formulation," T. Wagersreiter and S. Mukamel, *J. Chem. Phys.* **105**, 7997-8010 (1996).
28. "Chemical Bonding and Size Scaling of Nonlinear Polarizabilities of Conjugated Polymers," S. Tretiak, V. Chernyak and S. Mukamel, *Phys. Rev. Lett.* **77**, 4656-4659 (1996).
29. "Recursive Density-Matrix-Spectral-Moment Algorithm for Molecular Nonlinear Polarizabilities," S. Tretiak, V. Chernyak and S. Mukamel, *J. Chem. Phys.* **105**, 8914-8928 (1996).
30. "Electronic-Oscillator Analysis of Femtosecond Four-wave Mixing in Conjugated Polyenes," T. Meier, S. Tretiak, V. Chernyak, and S. Mukamel, *Phys. Rev. B* **55**, 4960-4977 (1997).
31. "Time-Frequency and Coordinate-Momentum Wigner Wavepackets in Nonlinear Spectroscopy," S. Mukamel, C. Ciordas-Ciurdariu, and V. Khidekel, *Adv. Chem. Phys.* **101**, 345-371 (1997).

32. "Probing the Two-Exciton Manifold of Light-Harvesting Antenna Complexes Using Femtosecond Four-Wave Mixing Spectroscopies," O. Kuhn and S. Mukamel, *J. Phys. Chem.* **101**, 809-816 (1997).
33. "Real-Space Density Matrix Description of Dynamic Correlations in the Optical Response of Many-Electron Systems," V. M. Axt and S. Mukamel, *In Nonlinear Optical Materials, IMA Volumes in Mathematics and Its Applications*, **101**, 33-47, J.V. Moloney, Editor, Springer-Verlag, Berlin (1998).
34. "Influence of a Phonon Bath on Electronic Correlations and Optical Response in Molecular Aggregates," V. M. Axt and S. Mukamel, *In Nonlinear Optical Materials, IMA Volumes in Mathematics and Its Applications*, **101**, 1-32, J.V. Moloney, Editor, Springer-Verlag, Berlin (1998).
35. "Coherent Versus Incoherent Energy Transfer in Light Harvesting Antenna Complexes," V. M. Axt, O. Kuhn, and S. Mukamel, *J. Lum.* **72-74**, 806-808, (1997).
36. "Density-Matrix-Electronic-Oscillator Representation of Optical Spectroscopy of Semiconductor Nanocrystals," S. Yokojima, T. Meier, and S. Mukamel, *J. Chem. Phys.* **106**, 3837-3853 (1997).
37. "Electronic Coherence and Collective Optical Excitations of Conjugated Molecules," S. Mukamel, S. Tretiak, T. Wagersreiter, and V. Chernyak, *Science* **277**, 781-787 (1997).
38. "Liouville-Space Pathways and Phase-Space Wavepackets in Femtosecond Spectroscopy," S. Mukamel, in *Nobel Symposium 101: Femtochemistry and Femtobiology - Ultrafast Dynamics at Atomic-Scale Resolution*, V. Sundstrom, Editor, Imperial College Press (1997).
39. "Multiple Exciton Coherence Sizes in Photosynthetic Antenna Complexes Viewed by Pump-Probe Spectroscopy," T. Meier, V. Chernyak and S. Mukamel, *J. Phys. Chem..B* **101**, 7332-7342 (1997).
40. "Polarons, Localization and Excitonic Coherence in Superradiance of Biological Antenna Complexes," T. Meier, Y. Zhao, V. Chernyak, and S. Mukamel, *J. Chem. Phys.*, **107**, 1-18, (1997).
41. "Femtosecond Photon Echoes in Molecular Aggregates," T. Meier, V. Chernyak, and S. Mukamel, *J. Chem. Phys.* **107**, 8759-8774 (1997).
42. "Wigner Spectrogram Representations of Hetrodyne-Detected Four-Wave-Mixing and Fluoresence Up-Conversion," S. Mukamel *J. Chem Phys.* **107**, 4165-4171 (1997).
43. "Two-Dimensional Real-Space Analysis of Optical Excitations in Acceptor-Substituted Carotenoids," S. Tretiak, V. Chernyak, and S. Mukamel, *J. Am. Chem. Soc.* **119**, 11408-11419 (1997).
44. "Real-Space Analysis of Electronic Excitations in Free-Base (H_2P) and Magnesium (MgP) Porphins," S. Tretiak, V. Chernyak, and S. Mukamel, *Chem. Phys. Lett.*, **297**, 357-364 (1998).
45. "Structure Determination of Antenna Complexes Using Two-Dimensional Femtosecond Electronic Spectroscopies," S. Mukamel, W. M. Zhang, and V. Chernyak, in *Photosynthesis: Mechanisms and Effects*, G. Garab, Ed., Kluwer, Dordrecht, **1**, 3-8, (1998).
46. "Nonlinear Optics of Semiconductor and Molecular Nanostructures; A Common Perspective," V. M. Axt and S. Mukamel, *Rev. Mod. Phys.* **70**, 145-174 (1998).
47. "Origin, Scaling and Saturation of Second Order Polarizabilities in Donor/Acceptor Polyenes," S. Tretiak, V. Chernyak, and S. Mukamel, *Chem. Phys. Lett.* **287**, 75-82 (1998).
48. "Solvent Reorganization in Long-Range Electron Transfer; Density Matrix Approach," by: A. Okada, V. Chernyak and S. Mukamel, *J. Phys. Chem* **102**, 1241-1251 (1998).

49. "Simulation of Three-Pulse-Echo and Fluorescence Depolarization in Photosynthetic Aggregates," W. M. Zhang, T. Meier, V. Chernyak and S. Mukamel, *Phil. Trans. Royal Soc. A* **356**, 405-419 (1998).
50. "Multidimensional Femtosecond Spectroscopies of Vibrational Motions in Liquids: Semiclassical Expansion," V. Chernyak and S. Mukamel *J. Chem. Phys.* **108**, 5812-5825 (1998).
51. "Exciton-Migration and Three-Pulse Femtosecond Optical Spectroscopy of Photosynthetic Antenna Complexes," W. M. Zhang, T. Meier, V. Chernyak, and S. Mukamel, *J. Chem. Phys.* **108**, 7763-7774 (1998).
52. "Effective Frenkel Hamiltonian for Optical Nonlinearities in Semiconductors: Application to Magnetoexcitons," V. Chernyak, S. Yokojima, T. Meier, and S. Mukamel, *Phys. Rev. B* **58**, 4496-4516 (1998).
53. "Stilbenoid Dimers: Dissection of a Paracyclophane Chromophore", G. Bazan, W. Oldham, R. Lachicotte, S. Tretiak, V. Chernyak, and S. Mukamel, *J. Am. Chem. Soc.* **120**, 9188-9204 (1998). "Localized Electronic Excitations in Phenylacetylene Dendrimers," S. Tretiak, V. Chernyak, and S. Mukamel, *J. Phys. Chem. B* **102**, 3310-3315 (1998).
54. "Excitonic-Interactions and Stark Spectroscopy of Light Harvesting Systems," O. Somsen, V. Chernyak, R. Frese, R. van Grondelle and S. Mukamel *J. Phys. Chem. B*, **102**, 8893-8908 (1998).
55. "Collective Coordinates for Semiclassical Femtosecond Dissipative Dynamics in Liouville Space," V. Chernyak and S. Mukamel, *J. Lum.* **76&77**, 15-21 (1998).
56. "Spin versus Boson Baths in Nonlinear Spectroscopy", Y. Zhao, V. Chernyak and S. Mukamel, *J. Phys. Chem. A* **102**, 6614-6634 (1998).
57. "Two-Dimensional Raman-Echo Spectroscopy; Femtosecond View of Vibrational Coherence," A. Piryatinski, V. Chernyak, and S. Mukamel, in *Ultrafast Phenomena XI*, edited by T. Elsaesser, J. G. Fujimoto, D. A. Wiersman, and W. Zinth (Springer Verlag, Berlin) 541-543, (1998).
58. "Two-Dimensional Femtosecond Spectroscopies of Coupled Chromophores," W. M. Zhang, V. Chernyak, and S. Mukamel, in *Ultrafast Phenomena XI*, edited by T. Elsaesser, J. G. Fujimoto, D. A. Wiersma, and W. Zinth, (Springer Verlag, Berlin) 663-665, (1998).
59. "Multidimensional Femtosecond Spectroscopies of Molecular Aggregates and Semiconductor Nanostructures; The Nonlinear Exciton Equations," V. Chernyak, W. M. Zhang and S. Mukamel, *J. Chem. Phys.* **109**, 9587-9601 (1998).
60. "Excited Electronic States of Carotenoids; Time-Dependent Density-Matrix-Response Algorithm," S. Tretiak, V. Chernyak and S. Mukamel *Intl. J. Quant. Chem.* **70**, 711-727 (1998).
61. "Optical Response Functions for Condensed Systems with Linear and Quadratic Electron-Vibration Coupling," M. Toutounji, G. J. Small, and S. Mukamel, *J. Chem. Phys.* **109**, 7949-7960 (1998).
62. "Lanczos Algorithm for Electron Transfer Rates in Solvents with Complex Spectral Densities," A. Okada, V. Chernyak, and S. Mukamel, in *Adv. Chem. Phys.*, Wiley, New York, **106**, 515-551, (1999).
63. "Femtosecond Four-Wave Mixing Spectroscopy of Magnetoexcitons in Semiconductor Quantum Wells," S. Yokojima, T. Meier, V. Chernyak, and S. Mukamel, *Phys. Rev. B*, **59**, 12584-12597 (1999).
64. "Complete Determination of Relaxation Parameters from Two-Dimensional Raman Spectroscopy," V. Chernyak, A. Piryatinski, and S. Mukamel, *Laser Chem.* **19**, 109-116 (1999).

65. "Two-Dimensional Raman Echoes; Femtosecond View of Molecular Structure and Vibrational Coherence", S. Mukamel, A. Piryatinski, and V. Chernyak, *Acct. Chem. Res.* **32**, 145-154 (1999).
66. "Nonlinear Optical Response Functions for a Chromophore with Linear and Quadratic Electron-Vibration Coupling," M. Toutounji, G. J. Small, and S. Mukamel, *J. Chem. Phys.*, **110**, 1017-1024 (1999).
67. "Multidimensional Femtosecond Correlation Spectroscopies of Electronic and Vibrational Excitons," W.M. Zhang, V. Chernyak, and S. Mukamel, *J. Chem. Phys.*, **110**, 5011-5028 (1999).
68. "Femtosecond Four-Wave Mixing Spectroscopy of Magnetoexcitons in Semiconductor Quantum Wells," S. Yokojima, T. Meier, V. Chernyak, and S. Mukamel, *Phys. Rev. B*, **59**, 12584-12597(1999).
69. "Intraband Terahertz Emission from Coupled Semiconductor Quantum Wells; Exciton Representation," W. M. Zhang, T. Meier, V. Chernyak, and S. Mukamel, *Phys. Rev. B*, **60**, 2599-2609 (1999).
70. "Semiclassical Effective Hamiltonian for Coupled Electronic and Nuclear Optical Response," V. Chernak, S. Tretiak, E. V. Tsiper, T. Meier, and S. Mukamel, Proc. of XXII Int'l. Workshop on Condensed Matter Theories, Vanderbilt University, D. Ernst, Editor (In Press).
71. "Ground-State-Density Matrix Algorithm for Excited State Adiabatic Surfaces; Application to Polyenes", E.V. Tsiper, V. Chernyak, S. Tretiak and S. Mukamel, *Chem. Phys. Lett*, **302**, 77-84 (1999).
72. "Superradiance Coherence Sizes in Single Molecule Spectroscopy of LH2 Antenna Complexes", Y. Zhao, T. Meier, W. Zhang, V. Chernyak and S. Mukamel, *J. Phys. Chem.*, **103**, 3954-3962 (1999).
73. "Electron Screening in Second Order Optical Polarizabilities of Elongated Donor/Acceptor Polyenes", S. Tretiak, V. Chernyak and S. Mukamel, *Chem. Phys.*, **245**, 145-163 (1999).
74. "Size Scaling of Third-Order Off-Resonant Polarizabilities; Electronic Coherence in Organic Oligomers," M. Schulz, S. Tretiak, V. Chernyak, and S. Mukamel, (1999) *J. Am. Chem. Soc.* (In Press).
75. "Stochastic-Trajectories and Non-Poisson Kinetics in Single-Molecule Spectroscopy." V. Chernyak, M. Schultz and S. Mukamel, *J. Chem. Phys.* **111**, 7416-7425 (1999).
76. "Two-Exciton States and Spectroscopy of Phenylacetylene Dendrimers", V. Chernyak, E. Y. Poliakov, S. Tretiak and S. Mukamel, *J. Chem. Phys.*, **111**, 4158-4168 (1999).
77. "Size Scaling of Third-Order Off-Resonant Polarizabilities; Electronic Coherence in Organic Oligomers," M. Schulz, S. Tretiak, V. Chernyak, and S. Mukamel, *J. Am. Chem. Soc.*, **112**, 452-459 (1999).
78. "Stochastic-Trajectories and Non-Poisson Kinetics in Single-Molecule Spectroscopy." V. Chernyak, M. Schultz and S. Mukamel, *J. Chem. Phys.* **111**, 7416-7425 (1999).
79. "Two-Exciton States and Spectroscopy of Phenylacetylene Dendrimers", V. Chernyak, E. Y. Poliakov, S. Tretiak and S. Mukamel, *J. Chem. Phys.*, **111**, 4158-4168 (1999).
80. "Excitonic Couplings and Electronic Coherence in Bridged Naphthalene Dimers," S. Tretiak, W.-M. Zhang, V. Chernyak, and S. Mukamel, *Proc. Nat. Acad. Sci.*, **96**, 13003-13008 (1999).
81. "Frenkel-exciton Hamiltonian for Dendrimeric Nanostar." T. Minami, S. Tretiak, V. Chernyak, and S. Mukamel, *J. Lum.*, **87-89**, 115-118 (1999).
82. "Simulations of Two-Dimensional Femtosecond Infrared Photon-Echoes of Glycine Dipeptide," A. Piryatinski, S. Tretiak, V. Chernyak and S. Mukamel, *J. Raman Spec.*, **31**, 125-135 (2000).

83. "Electronic versus Vibrational Optical Nonlinearities of Push-Pull Polymers", V. Chernyak, S. Tretiak, and S. Mukamel, *Chem. Phys. Lett.*, **319**, 261-264 (2000).

PERSONNEL SUPPORTED

Research Associates:

Dr. A. Okada, Institute of Molecular Science Okazaki
 Dr. E. Poliakov, University of New Mexico
 Dr. E. Tsiper, University of Utah
 Dr. L. A. Leegwater,
 Dr. M. Hartmann, Max-Planck-Arbeitsgruppe, Germany
 Dr. L. Belleguie, Institut fuer Theoretische Physik II, Germany
 Dr. A. Takahashi, Kyoto University, Japan
 Dr. G. Chen, California Institute of Technology
 Dr. V. Khidekel, Tel Aviv University, Israel
 Dr. T. Wagersreiter, Institut fur Physikalische Chemie, Austria
 Dr. D. Beljonne, University of Mons, Belgium
 Dr. T. Meier, Phillips University, Germany
 Dr. O. Kuhn, Deutscher Akademischer Austauschdienst, Germany,
 Dr. V. M. Axt, Institut fuer Theoretische Physik II, Germany
 Dr. S. Yokojima, University of Hong Kong
 Dr. Y. Zhao, University of Hong Kong
 Dr. A. Piryatinski, University of Rochester
 Dr. M. Schulz, University of Freiburg, Germany

Visiting Scientists:

Dr. V. Chernyak, Ph. D., USSR Academy of Sciences
 Dr. O. Somsen, Free University of Amsterdam, The Netherlands

Graduate Students Supported:

Mr. S. Tretiak, Department of Chemistry, University of Rochester
 Mr. W. M. Zhang, Department of Chemistry, University of Rochester
 Mr. Y. Maruyama, Visiting student from the Institute of Molecular Science Okazaki
 Mr. N. Wang, Department of Chemistry, University of Rochester
 Mr. C. Ciordas-Ciurdario, Department of Chemistry, University of Rochester
 Mr. M. Toutounji, Visiting student from Northwestern University
 Mr. P. Rott, Department of Chemistry, University of Rochester

Undergraduate Students:

None

In addition, we are continuing to collaborate with these former Postdoctoral Fellows: Dr. Martin Axt, who currently holds a faculty position at the Institut fuer Theoretische Physik II Westfaelische Wilhelms-Universitaet Muenster; Dr. Torsten Meier, Phillips University, Marburg; Dr. Guanhua Chen, Hong Kong University of Science

INTERACTIONS/TRANSITIONS

a. Participation/Presentation at Meetings, Conferences, Seminars, etc.

INVITED PRESENTATIONS

Seminar on "Nonlinear Optical Spectroscopy of Confined Excitons in Conjugated Polyenes and Molecular Nanostructures," Department of Chemistry, Pennsylvania State University, January 1996.

Air Force Nonlinear Optical Polymers Contractors Review Meeting, Fairborn, OH, "Electronic Oscillator Approach to Optical Nonlinearities in Conjugated Polymers," February 1996.

Workshop on Materials for Nonlinear Optics Applications, Institute for Mathematics and Its Applications at the University of Minnesota, "Optical Nonlinearities of Confined Excitons in Molecular Nanostructures and Conjugated Polyenes," March 1996.

Condensed Matter Seminar on "Oscillator, Quasiparticle Representation of Femtosecond Nonlinear Spectroscopy in Condensed Phases," Department of Physics, University of California, Berkeley, April 1996.

Physical Chemistry Seminar on "Electronic Coherence and Multidimensional Optical Spectroscopy of Conjugated and Nonconjugated Molecular Materials," Department of Chemistry, University of California, Berkeley, April 1996.

Seminar on "Collective Electronic Oscillators and Nonlinear Optical Spectroscopy of Conjugated Polyenes and Molecular Aggregates," Department of Chemistry, Stanford University, Stanford, CA, April 1996.

Seminar on "Femtosecond Spectroscopy of Molecular Aggregates, conjugated Polyenes and Liquids; Molecular Dynamics in Liouville Space," Department of Chemistry, California Institute of Technology, April 1996.

Discussion Leader, Gordon Conference on Electronic Processes in Organic Materials, Proctor Academy, Andover, New Hampshire, July 1996.

Tutorial Course at the XVth International Conference on Raman Spectroscopy, (ICORS 96), University of Pittsburgh, Pennsylvania, August 1996.

International Conference on Luminescence (ICL 96), Prague, "Collective Electronic Oscillators for Nonlinear Spectroscopy of Conjugated Molecules and Antennae Complexes" August 1996.

Nobel Symposium on Femtochemistry and Femtobiology: Ultrafast Reaction Dynamics at Atomic-Scale Resolution, "Liouville-Space Pathways and Phase-Space Wavepackets in Femtosecond Spectroscopy." Björkborn, Sweden, September 1996.

Workshop on Light Harvesting Physics, Lithuania, . "Nonlinear Spectroscopy of the Photosynthetic Antenna Systems," September 1996.

International Workshop on X-ray Free Electron Laser Applications, Hamburg "Density Matrix Representations of Optical Nonlinearities in Molecular Materials," September 1996.

Colloquium Department of Chemistry, University of Chicago, "Electronic Coherence and Collective Excitations in Nonlinear Spectroscopy of Conjugated Molecules, Biological Complexes and Semiconductor Nanoparticles." November 1996.

Femtochemistry III - 97, Lund, Sweden, "Ultrafast Spectroscopy of Confined Excitons in Biological Complexes and Conjugated Polyenes," August 1997.

Lund University, Sweden, "Electronic Coherence and Collective Optical Excitations of Conjugated Molecules and Biological Complexes," August 1997.

Universität Würzburg, Department of Physics, Germany, "Multidimensional Femtosecond-Spectroscopy of Nuclear Dynamics in Liquids," October 1997.

Universität Ulm, Department of Physics, Germany, "Collective Excitations in Nonlinear Spectroscopy of Conjugated and Aggregated Molecules," October 1997.

Max-Planck Institute for Solid State Physics, Stuttgart, Germany, "Collective Excitations in Nonlinear Spectroscopy of Conjugated and Aggregated Molecules," October 1997.

Institut für Physikalische und theoretische Chemie der Technischen Universität München, Germany, "Multidimensional Femtosecond-Spectroscopy of Nuclear Dynamics in Liquids," November 1997.

University of Utrecht Institute of Theoretical Physics, Netherlands, Physics Colloquium, "Collective Electronic Excitations of Molecular Nanostructures and Biological Complexes," November 1997.

University of Leiden, Netherlands, Biophysics Seminar, "Collective Electronic Excitations of Molecular Nanostructures and Biological Complexes," November 1997.

University of Groningen, Netherlands, "Collective Electronic Excitations of Molecular Nanostructures and Biological Complexes," November 1997.

Max-Planck-Institut Für Quantenoptik, Munich, Germany, "Electronic Coherence and Collective Optical Excitation of Conjugated Molecules," November 1997.

European Laboratory for Non-Linear Spectroscopy, (LENS), University of Firenze, Italy, "Collective Electronic Excitations of Molecular Nanostructures and Biological Complexes," November 1997.

Dipartimento di Chimica Industriale e Ingegneria Chimica "Giulio Natta" Politecnico di Milano, Italy, "Collective Electronic Excitations of Molecular Nanostructures and Biological Complexes," November 1997.

Scuola Normale Superiore Di Pisa, Italy, "Collective Excitations in Nonlinear Spectroscopy of Conjugated and Aggregated Molecules," November 1997.

Universität Wien, Department of Chemistry, Austria, "Collective Optical Excitations in Non-linear Spectroscopy of Conjugated Molecules and Semiconductor Nanocrystals," November 1997.

Vanderbilt University, Nashville, TN, Physics Colloquium, "Collective Oscillator Approach to Optical Nonlinearities of Conjugated Molecules and Semiconductor Nanoparticles," January 1998.

SPIE Symposium, San Jose, California, Laser Techniques for Condensed Phase and Biological Systems, "Femtosecond Spectroscopy of Biological Complexes and Conjugated Molecules," January, 1998.

Optical Society of America, Coeur d'Alene, Idaho, Workshop on Radiative Processes and Dephasing in Semiconductors, "Collective Excitations in Non-Linear Spectroscopy of Nanostructures," February 1998.

Thirty-Eighth Sanibel Symposium, St. Augustine, Florida, "Femtosecond Spectroscopy of Confined Excitons in Conjugated Molecules and Biological Complexes," February, 1998.

American Physical Society National Meeting, Los Angeles, CA, "Multidimensional Femtosecond Spectroscopy of Nuclear Dynamics in Liquids," March 1998.

Workshop on Transport in Organic Materials II, University of New Mexico, Albuquerque, New Mexico, "Excitonic Transport in Femtosecond Spectroscopy of Molecular and Biological Complexes," March, 1998.

University of Wisconsin-Madison, Samuel M. McElvain Lecture, "Collective Excitations In Femtosecond Spectroscopy of Conjugated Molecules and Biological Complexes," May, 1998.

Molecular Dynamics, Contractor's Review, Air Force Office of Scientific Research, Naval Postgraduate School, Monterey, CA, "Collective Electronic Excitations in Nonlinear Spectroscopy of Conjugated and Aggregated Molecules," May, 1998.

XXII International Workshop on Condensed Matter Theories, Vanderbilt University, Nashville, TN, "Collective Electronic Excitations in Nonlinear Spectroscopy of Conjugated Molecules and Biological Complexes," June, 1998.

- XVI International Conference on Coherent And Nonlinear Optics (ICONO '98), Moscow, "Collective Electronic Excitations in Nonlinear Spectroscopy of Conjugated Molecules and Biological Complexes," June, 1998.
- Free University of Berlin, Institute for Physical and Theoretical Chemistry, Berlin Germany, "Multidimensional Correlation Spectroscopy: Femtosecond View Of Electronic Coherence," July, 1998.
- University of Frankfurt, Institute for Theoretical Physics, Frankfurt, Germany, "Multidimensional Femtosecond Correlation Spectroscopy of Conjugated Molecules and Biological Complexes," July, 1998.
- XI International Conference on Ultrafast Phenomena, Garmisch, Germany, "Two-Dimensional Raman Echo Spectroscopies: Femtosecond View of Vibrational Coherence," July, 1998.
- XI International Congress on Photosynthesis, Budapest, Hungary, "Femtosecond Nonlinear Spectroscopy and Electronic Coherence Sizes Of Antenna Complexes," August, 1998.
- Photosynthetic Antenna Structures Satellite Meeting, Tata, Hungary, "Multidimensional Femtosecond Correlation Spectroscopies of Photosynthetic Antennae," August, 1998.
- Electronic Coherence Sizes Of Antenna Complexes," August, 1998.
- University of Utah, Physics Colloquium, "Collective Electronic Excitations and Nonlinear Spectroscopy of Conjugated Molecules and Biological Complexes." September, 1998.
- Optical Society of America National Meeting, Baltimore MD, Symposium on Ultrafast Coherence Spectroscopy, "Time-Frequency and Coordinate-Momentum Wigner Spectrograms in Nonlinear Spectroscopy," October, 1998.
- University of Toronto, Department of Physics, Toronto, Canada, "Collective Electronic Excitations in Femtosecond Spectroscopy of Conjugated Molecules and Biological Complexes", November, 1998
- MRS Fall Symposium, Dynamics in Small Confining Systems V, Boston, MA, "Localized Optical Excitations and Two-Exciton Spectroscopy of Phenylacetylene Dendrimers," December, 1998.
- 29th Winter Colloquium on the Physics of Quantum Electronics, Snowbird, Utah, "Nonlinear Femtosecond Spectroscopy of Confined Excitons: Beyond the Local Field Approximation", January, 1999.
- Pacific Northwest National Laboratory, Environmental Molecular Sciences Lab., Richland, WA, " Multidimensional Spectroscopy of Conjugated Molecules and Biological Complexes. January, 1999.
- Linear Coherent Light Source Workshop, at Stanford Linear Accelerator Center, Stanford University, Stanford, CA, "Femtosecond Coherent X-Ray Spectroscopy", January, 1999.
- University of Michigan, Chemistry Colloquium, "Collective Electronic Excitations and Multidimensional Femtosecond Spectroscopy of Conjugated Molecular Nanostructures and Biological Complexes", January, 1999.
- Free University of Amsterdam, Biophysics Seminar, "Multidimensional Femtosecond Spectroscopy of Photosynthetic Aggregates and Molecular Vibrations", January 1999.
- University of Groningen, Physical Chemistry Seminar, "Multidimensional Femtosecond Spectroscopy of Photosynthetic Aggregates and Molecular Vibrations", January 1999.
- Harvard University - MIT, Lecture, "Multidimensional Correlation Spectroscopy: Femtosecond View of Electronic Coherence in Conjugated Biological Complexes", March 1999.
- American Physical Society, Centennial Meeting, Atlanta, Georgia, "Scaling Properties and Two-Exciton Spectroscopy of Supermolecular Dendrimers", March 1999.

b. Consultative and advisory functions

Advisory panel for DESY, workshop on "x-ray scattering from electron systems in the field of coherent radiation" to be held in Hamburg, September 17 and 18, 1996.

c. Transitions. Cases where knowledge resulting from your effort is used, or will be used

We started a collaboration with Dr. Ruth Pacher's group at Wright Patterson to combine our oscillator procedure to ab initio calculations. We also discussed the possibilities of calculating resonant saturation effects in $\chi^{(3)}$ of conjugated polyenes.

NEW DISCOVERIES, INVENTIONS, OR PATENT DISCLOSURES

None at this time

HONORS/AWARDS

Fellow of the American Physical Society (elected 1987)

Fellow of the Optical Society of America (elected 1989)

Editorial Board of Oxford University Press for the series on Mesoscopic Physics and Nanotechnology, (1995-1997)

Advisory Editorial Board of Chemical Physics Letters (1996-98)

Miller Fellowship at the Departments of Chemistry and Physics, University of California, Berkeley (1996)

Advisory board of the Ultrafast Phenomena Tenth International Meeting (1996)

Guggenheim Fellow (1996)

The Raymond and Beverly Sackler Lectureship, Tel Aviv University (1997)

Alexander von Humboldt Research Award for Senior US Scientists (1997)

Nominating Committee for the Division of Chemical Physics APS (1997)

Chair of Gordon Conference on Electronic Processes in Organic Materials, Newport, RI (1998)

General Co-Chair, Ultrafast Phenomena XII (2000)